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Development of biodiesel: Current scenario

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ABSTRACT

Fuels are inevitable for industrial development and growth of any country. The life span of fossil fuel resources has always been terrifying. Biodiesel, a renewable source of energy seems to be an ideal solution for global energy demands including India as well. The current review is addressed to various aspects of biodiesel production. Latest literature has been critically reviewed and consulted.

Contents

1. Introduction

The World Energy Forum has predicted that fossil-based oil, coal and gas reserves will be exhausted in less than another 10 decades. In Indian scenario, the data available from auto fuel consumption reveals that in the year 2004, 9 million metric tonnes (MMT) petrol and 42 MMT of diesel were consumed with a crude oil import amounting to rupees 1,10,000 crores [1]. However, this is a global issue. Mankind is so much dependent on fossil fuels that it is beyond imagination to think a world without them. But the scenario anticipated is a reality. As the fossil fuels are limited and it takes million of years for their formation, their availability may be prolonged by decreasing overall consumption. Various renewable sources of energy have successfully been tried and used by different nations to limit the use of fossil fuels. This renewable source of energy includes solar energy, wind energy, geothermal energy, tidal energy, ocean thermal energy, hydropower and others. Table 1 depicts the renewable energy potential of India and

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Table 1
Potential and production of renewable energy for various sources in India

Source/systems	Estimated potential (MW)	Cumulative installed capacity (as on 31 March 2005) (MW)
Solar photovoltaic	20 MW/km^2	2.80
Wind power	45,000	3595.00
Biomass power	16,000	302.53
Bagasse Co-generation	3,500	447.00
Waste to energy		
Municipal solid waste	1,700	17.00
Industrial waste	1,000	29.50
Small hydropower (up to 25 MW)	15,000	1705.63
Total		6099.46

Table 2
Top 10 countries in terms of absolute biodiesel potential

Rank	Country	Volume potential (L)	Production ($/L)[a]
1	Malaysia	14,540,000,000	$0.53
2	Indonesia	7,595,000,000	$0.49
3	Argentina	5,255,000,000	$0.62
4	USA	3,212,000,000	$0.70
5	Brazil	2,567,000,000	$0.62
6	Netherlands	2,496,000,000	$0.75
7	Germany	2,024,000,000	$0.79
8	Philippines	1,234,000,000	$0.53
9	Belgium	1,213,000,000	$0.78
10	Spain	1,073,000,000	$1.71

[a] Average production cost per liter is calculated from all available lipid feedstock prices, increased by a $0.12 refining cost and decreased by $0.04 for the sale of by-products.

the resources tapped till 2005 [2]. Use of the renewable energy has made the nation self-dependent to some extent but still it is far behind to make a significant difference in import of crude oil, which is the need of present day. In India, the domestic production of crude oil in year 2003–2004 was 33.38 million tonnes, whereas, 90.43 million tonnes oil (which amounts to 73% of total oil consumed) were imported [3]. A new technology, i.e. transesterification reaction has been applied to produce a renewable fuel "biodiesel" derived from various raw materials. These raw materials include both the edible and non-edible oils, algae, waste cooking oil, etc. It is named biodiesel because it is derived from biological products and matches petrodiesel in performance. The biodiesel so produced has lesser exhaust emissions in terms of unburnt hydrocarbon, carbon monoxide and particulate matter. Biodiesel can be termed clean fuel as it does not contain carcinogens and its sulphur content is also lesser than the mineral diesel. It possesses high biodegradability and lubricating property which makes it even better fuel. Hence, being a renewable fuel and characteristics similar to petrodiesel, it has the potential to be an alternate for petrodiesel in long run. However, few other properties of biodiesel are of concern and have to be improved to make it usable in neat form (i.e. 100% biodiesel). These properties are, increase in calorific value, engine power; reduced emission of NO_x, and improvement in low temperature properties [4]. An improvement in oxidation stability is also desired to prevent it from deterioration with time. At present it is compatible in blended form with mineral diesel in the ratio 20 (biodiesel):80 (mineral diesel). Biodiesel has been in use in countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European nations. However, the potential for its production and application is much more. Table 2 depicts the list of top 10 nations in terms of absolute biodiesel production potential with Malaysia far ahead among the rest [5]. The feedstock available for development of biodiesel in these nations is 28% for soybean oil, 22% for palm oil, 20% for animal fats, 11% for coconut oil, while rapeseed, sunflower and olive oils constitute 5% each.

2. History of biodiesel development

Prior to biodiesel, biofuel was developed by Rudolph Diesel, the inventor of compression ignition (CI) engine in 1900. Peanut oil was used as a fuel to run the diesel engine. At that time, crude oil was available in plenty and was just refined to run the diesel engines. Hence, vegetable oils got neglected as a source of fuel. But, in recent times, due to realization that crude oil is limited and poses threat to well being of mankind from emissions of exhaust gases, vegetable oil has been revisited for its scope as a fuel in CI engines. However, due to high viscosity and low volatility, its long-term use posed different problems such as deposition, ring sticking and injector choking in engine [6]. Hence, improvement in the vegetable oil was foreseen to improve the quality of the fuel. To lower the viscosity of vegetable oil, chemical and thermal processes were tried to make vegetable oil compatible with CI engines. The well-known thermal process, pyrolysis, resulted in production of low value materials and sometimes resulted in more production of gasoline instead of diesel. Other processes, i.e. blending and microemulsification of vegetable oils reduced the viscosity but still posed few problems. These problems were namely carbon deposition and lubricating oil contamination. Hence, the most suitable process for reducing the viscosity found was the chemical process, transesterification, where triglycerides from vegetable oils react with a lower alcohol to produce fatty acid alkyl esters possessing properties similar to mineral diesel [7].

3. Raw materials for biodiesel production

Raw materials contribute to a major portion in the cost of biodiesel production. The choice of raw materials depends mainly on its availability and cost. Countries such as USA and those belonging to European community are self-dependent in production of edible oils and even have surplus amount to export. Hence, edible oils such as soybean and rapeseed are used in USA and European Nations, respectively. Similarly countries with coastal area such as Malaysia and Indonesia have surplus coconut oil and that is utilised for the synthesis of biodiesel [8]. Brazil, being the largest sugarcane producer in the world, produces ethanol which is used to run 40% of its fuel powered cars [9]. India even though with a vast land area including coastal area, does not produce enough edible oils and has to import them to meet the food requirements. Hence, in Indian context, the raw materials used for development of biodiesel have been the unutilised and underutilised materials. The raw materials used at present in India are, *Jatropha curcas* (jatropha) and *Pongamia pinnata* (karanja). Oils from both the plants contain toxins and hence are non-edible. Jatropha contains phorbol esters and curcin as toxins [1], whereas, karanja contains furanoflavones, furanoflavonols, chromenoflavones, flavones and furanodiketones as toxins which make the oil non-edible [10]. The oil content from the seed of plant oil varies. Seeds of soybean contain only 20% of oil, whereas, 40% of oil can be expelled from seeds of rapeseed [11]. Jatropha and karanja seeds possess 40% and 33% oil, respectively [12]. Search for raw material for biodiesel production is not limited to vegetable oils only. In United States, researchers are of the opinion that even surplus vegetable oils will not be enough to meet the future demand of biodiesel and hence have tried algae as a raw material for biodiesel production. Algae, in presence of sunlight, converts carbon dioxide into sugars and proteins. But, when they are starved of nitrogen, mainly oil is produced [13]. A microalgae *Chlorella protothecoides*, has been

grown under autotrophic and heterotrophic conditions to obtain lipid as raw material for biodiesel production. Lipid content in the heterotrophic cells reached 55.20% as compared to 14.57% in autotrophic cells. The microalgal oil as lipids was prepared by pulverization of heterotrophic cell powder in a mortar and extracted with *n*-hexane. The lipid was successfully used for biodiesel production [14]. Fargione et al. [15] suggested that cultivation of biofuel crops on existing rainforests, peatlands, savannas, or grasslands which is practised in Brazil, Southeast Asia and United States, produce more carbon dioxide than the actual reduction they bring by using them as an alternate fuel. This is being termed as 'biofuel carbon debt'. A more viable method suggested by them is the use of biofuels made from waste biomass or the use of degraded and waste land for their growth. Tilman et al. [16] suggest that more energy, greater green house reductions and less agricultural pollution per hectare than corn ethanol or soybean biodiesel can be achieved by biofuel synthesis from low-input high-diversity (LIHD) mixtures of grassland perennials. The authors emphasise wide exploration of LIHD biomass that can be produced on abandoned agricultural lands and will not disturb either the ecosystem or fertile soils. Koonin [17], in his editorial has reported that 2% of transportation fuels are biomass-based (ethanol or biodiesel) and are being used in blended form with fossil fuels. Ethanol is derived mainly from cane sugar and biodiesel from plant oils. Nations such as United States, European Union and India are exploring the possibilities to increase their road fuel to 5% by 2011.

4. Transesterification

Fuels derived from chemical and thermal processes are termed as biodiesels [6]. While thermal process had some limitations, the chemical process, i.e. transesterification, proved to be a better method. Simple process, easy operation and the by-products obtained in the form of glycerol make the process attractive and widely accepted. Transesterification has been described as a chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters that are termed as biodiesel [18]. Fig. 1 depicts the transesterification reaction [19].

An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include the type of catalyst, alcohol, water content in oil and the rate of stirring. Sharma and Singh [10] emphasised that mode of stirring is equally important, where better yield was obtained with mechanical stirring than with magnetic stirring.

Depending on the fatty acid composition of the oil, its saponification number (SN), iodine value (IV) and cetane number (CN); it can be determined at the starting stage, whether the oil is suitable for transesterification reaction or not. Azam et al. [12] thus chose 75 plant oils available in India and found their fatty acid composition, SN, IV and CN. On the basis of these parameters, 37 species showed the potential for development of biodiesel [12]. An inverse relationship exists between the oxidation stability and cold temperature properties of the biodiesel. Better stability of biodiesel is achieved with oil having more content of saturated fatty acids, which is attributed to their resistance to auto-oxidation. Whereas, presence of more percentage of unsaturated fatty acids is favoured for low temperature flow properties of the fluid such as cloud point, pour point and cold filter plugging point. Hence, depending upon the percent composition of saturates and unsaturates in the oil, one of the parameters among oxidation stability and cold temperature property of biodiesel has to be compromised [20]. It is also desired that the percent composition of linolenic acid and any acid containing four double bonds in esters should be within the limit of 12% and 1%, respectively [12]. Cetane number signifies the ignition delay time of the fuel on its injection into the combustion chamber. A higher CN of esters is desired, which is an indication of short ignition delay [21]. However, with an increase in CN, IV decreases. IV is an indication of the level of unsaturation and its lower value leads to solidification of esters at lower temperature. Hence, an upper limit of 65 has been specified in American Society for Testing and Materials (ASTM). The minimum value of CN assigned by US biodiesel standard is 47.

5. Variables affecting the transesterification reaction

Transesterification reaction is quite sensitive to various parameters. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimised. These parameters include free fatty acids (FFAs), water content, molar ratio of alcohol to oil, catalyst, reaction temperature and stirring. Each parameter is equally important to achieve a high quality biodiesel which meets the regulatory standards.

5.1. Free fatty acids

Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones [22]. Higher amount of free fatty acids leads to higher acid value. Vegetable oils should have free fatty acids within a desired limit for alkaline transesterification, beyond which either the reaction will not take place or the yield will be too less. Table 3 [7,18,23–27] depicts the level of FFA worked out by researchers. It is clear from the table that the FFA level in the oil should be below a desired level (ranging from less than 0.5% to less than 3%) for alkaline transesterification to take place.

The application of the acid catalyst is to reduce the free fatty acids to a level safe enough for alkali transesterification. Else, the product formed will be soap instead of esters. During acid catalysed process, the FFA react with alcohol to produce esters but simultaneously, water is also produced which inhibits the transesterification reaction [28]. An alkali catalyst proceeds at around 4000 times faster than with the same amount of acid catalyst and hence is preferred over the acid catalyst after the acid value is reduced to the desired limit [29]. Hence, the transesterification reaction is one-step process for oils with FFA within the range and is a two-step process for oils with FFA exceeding the range. In a two-step process, acid esterification is followed by alkali transesterification.

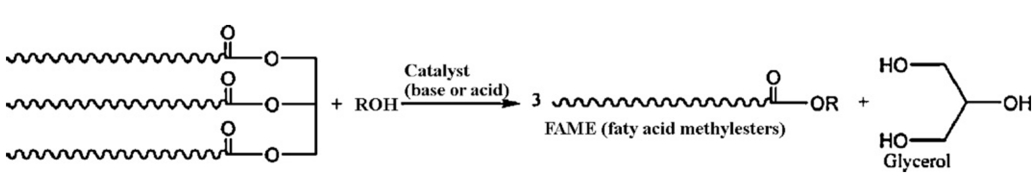


Fig. 1. Transesterification reaction of triglycerides.

Table 3
Level of FFA recommended for alkaline transesterification

Author	FFA recommended (%)	Reference
Ma and Hanna	<1	[7]
Ramadhas et al.	≤2	[18]
Canakci and Van Gerpan	<3	[23]
Zhang et al.	<0.5	[24]
Freedman et al.	<1	[25]
Tiwari et al.	<1	[26]
Sahoo et al.	≤2	[27]

5.2. Water content

The raw materials being used as starting material should be free from water content. Water content as low as 0.1% has been reported to decrease the conversion of ester to a significant extent [28]. Srivastava and Verma [30] reported the removal of the moisture content by heating the oil in an oven for 1 h at 110 °C before starting the transesterification reaction. Meher et al. [31] dissolved the catalyst, potassium hydroxide in methanol just before starting the transesterification reaction in an attempt to prevent the moisture absorbance.

5.3. Alcohol and molar ratio employed

Lower alcohols such as methanol, ethanol, propanol, etc. can be employed for transesterification reaction without any significant difference in the yield of the product. Methanol is toxic but is preferred among the others owing to its low cost. Ethanol is not preferred because of its low reactivity compared to methanol. Viscosity of ethyl esters is slightly higher and low temperature properties (cloud point, pour point) are slightly lower than those of methyl esters [32]. These findings make methanol more amenable for use as alcohol in biodiesel development. However, methanol has a lower boiling point of 64.7 °C and the transesterification reaction is carried out at a temperature which is near to this temperature. Vapours of methanol, which are highly toxic and can cause permanent blindness, are likely to be present near the site of reaction set up. Hence, appropriate measures have to be ensured for the safety of personnel working around. A new technique has been developed by the researchers [33] where alcohol in supercritical condition is used for the completion of transesterification reaction in shorter period of time without using any catalyst. The reason for the shorter time span is that the oil and supercritical alcohol exist in the same phase. In the supercritical transesterification method, a conversion of 50–95% was achieved in first 10 min. Presence of water was a source of interference in catalytic transesterification, whereas, the presence of water had shown a positive affect in methyl ester conversion by supercritical method [32].

The commonly employed molar ratio for two-step transesterification is 6:1 for acid transesterification and 9:1 for alkali catalysed transesterification. However, the optimum molar ratio has shown to differ a little depending on the raw oil taken and its acid value. For single step transesterification reaction, 10:1 molar ratio has been used more often, although an optimum molar ratio varying from 6:1 to 13:1 has been employed by other researchers [34]. A molar ratio higher than the optimum value reduces the yield and makes the separation process of esters and glycerol difficult. High molar (40:1) is needed where supercritical methanol is used for transesterification method [33].

5.4. Types and amount of catalysts

A catalyst is needed to improve the transesterification reaction and yield [35]. Homogeneous catalyst has been in use at present at industrial level for production of biodiesel. Sulphuric acid (H_2SO_4) is the commonly used catalyst during acid transesterification whereas sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the catalyst used for alkaline transesterification [34]. Sodium methoxide (CH_3ONa) and potassium methoxide (CH_3OK) are the other homogeneous catalyst which perform better than NaOH and KOH in terms of yield. Formation of small amount of water during the transesterification reaction results in lower yield of biodiesel with NaOH or KOH as a catalyst. Whereas, CH_3ONa or CH_3OK show higher yield because there is no water formation as by-product during the reaction [36]. Among KOH and NaOH, Vicente et al. [37] reported higher yield with KOH (91.67%) as compared to that of NaOH (85.9%). However, the purity of the ester reported was similar with these two catalysts. Contrary to this, Leung and Guo [36] have reported different amounts of catalysts required to achieve the same conversion of methyl esters. The amounts of catalysts required were 1.1, 1.3 and 1.5 wt.% for NaOH, CH_3ONa and KOH, respectively to get maximum conversion of methyl esters. This was attributed to the smallest molar mass of NaOH (40 g/mol) as compared to CH_3ONa (54 g/mol) and KOH (56 g/mol). The amount of acid catalyst, used to reduce the acid value ranges from 0.65% to 1.43% (v/v) H_2SO_4. However, the amount most commonly used by researchers is 1% (v/v) of 100% H_2SO_4. Optimum amount of H_2SO_4 as catalyst only is to be added, as higher volume may burn the oil and can darken the product. The amount of NaOH or KOH used during alkali catalysed transesterification reaction ranges from 0.7% to 1.5% by weight, depending on the nature of oil [34]. Lower amount of catalyst results in incomplete reaction, whereas higher amount of catalyst causes soap formation. Hence, an optimum amount of catalyst is a very important parameter in the transesterification reaction.

Homogeneous catalysts have few disadvantages in their application. These catalysts have to be removed from the final product with repeated washing with distilled water, which give rise to colossal generation of wastewater [38]. Heterogeneous type of catalysts have been tried to overcome the drawbacks of homogeneous catalysts. Heterogeneous catalysts can be separated from the reaction mixtures and reused. They also show less corrosive nature which makes them better alternative for homogeneous catalyst. Activated calcium oxide (CaO) was used as solid-based heterogeneous catalyst for eight runs without significant deactivation. Magnesium oxide, successfully used as catalyst for biodiesel development was found to be cost effective also. A simulation study by Dossin et al. [39] indicated 100,000 tonnes of biodiesel production per year with 5.7 tonnes of MgO as catalyst in a continuous stirred reactor of 25 m^3 capacity at 50 °C. WO_3/ZrO_2 and SO_4^{2-}/ZrO_2 catalysts have been used by Park et al. [40] as heterogeneous catalyst. SO_4^{2-}/ZrO_2 were not suitable because of the loss of SO_4^{2-} in liquid phase application. However, WO_3/ZrO_2 as a catalyst showed active and durable catalytic activity in the continuous flow process. Karmee and Chadha [41] used both homogeneous and heterogeneous catalysts for biodiesel development. 92% yield was obtained with the homogeneous catalyst, KOH under optimum conditions in 1.5 h reaction time. Whereas, comparatively lower yield of 83% was achieved with ZnO (a heterogeneous catalyst) in 24 h reaction time. Even lesser yield (47–59%) was achieved with other heterogeneous catalysts, Hβ-Zeolite and Montmorillonite. Anion-exchange resin has also been used as heterogeneous catalyst to achieve 98.8% purity of biodiesel. A three-step regeneration method augmented the reuse of the catalyst [42]. Acidic ion-exchange resins have been tried as catalysts to determine their efficiency on free fatty acid conversion. At optimum conditions, 45.7% FFA conversion has been reported [43].

5.5. Reaction temperature

As a general rule, transesterification reaction is tried to be accomplished at lowest possible temperature and time [44]. The commonly employed temperature ranges from as low as room temperature to up to 65 °C. Transesterification reaction has been reported to be influenced positively with increase in temperature. The boiling point of methanol is 64.7 °C and hence the transesterification reaction is carried out within this range as a temperature higher than this may burn methanol. Higher temperature also favours saponification and hence must be avoided [18]. Temperature of 350 °C has been considered to be optimum while using supercritical methanol [45].

5.6. Rate and mode of stirring

Scientific workers have reported stirring to be an equally important parameter for synthesis of biodiesel. Transesterification reaction was incomplete with 180 rotations per minute (rpm) of stirring, while the yield was same with 360 rpm and 600 rpm [31]. Mixing of reactants at 400 rpm with magnetic stirrer was performed by Veljkovic et al. [46] to get the optimum yield. A higher rate of stirring of 1100 rpm has also been reported to achieve maximum yield of biodiesel. Not much information on mode of stirring is available. However, a better yield with mechanical stirring has been reported than with magnetic mode of stirring [10,36].

5.7. Purification of the final product

The methyl esters obtained after one-step transesterification reaction were treated with hot water at 70 °C (1/5 of methyl ester volume) and 5% H_3PO_4 (aq) at 50 °C. After discharge of the wastewater, the ester layer was dried in vacuum and checked with ceric ammonium nitrate reagent for glycerol. Similar process was adopted for two-step transesterification method [19]. The fatty acid methyl esters were distilled by Wang et al. [47] at 180 °C under vacuum (40 ± 5 mmHg) and collected. The distillation was assumed to be completed when the temperature reached 240 °C (40 ± 5 mmHg) and the final yield obtained was 93.0 wt.%. Biodiesel separated after acidic transesterification was washed with petroleum ether and then with hot water (50 °C) until the washing reached a neutral pH. Srivastava and Verma [30] washed the biodiesel with 10% H_3PO_4 by bubble wash method after separation from glycerol. Biodiesel was further purified by passing air by aquarium stone for at least 24 h. The product biodiesel is also treated by washing it with hot distilled water to remove the dissolved impurities such as catalysts, alcohol, etc. Silica gel has been reported to be used for removing the catalyst from the biodiesel product [48].

The yield of biodiesel is calculated as follows [36]:

$$\text{Product yield} = \frac{\text{Wt. of product}}{\text{Wt. of raw oil}} \quad (1)$$

Conversion of triglyceride to alkyl ester is calculated by titration method [40], i.e. by measurement of acid value:

$$\text{Conversion}(\%) = \left[\frac{\text{Initial acid value} - \text{Final acid value}}{\text{Initial acid value}}\right] \times 100 \quad (2)$$

6. Conclusion

India is a vast country and is a booming economy. In XIth plan, a growth rate of more than 8.0% is envisaged. It could only be achieved by availability of enough energy. As fossil fuels are dwindling, development and application of biodiesel, that too from non-edible oils seems to be a solution. The review seems to highlight these aspects.

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